

Synthesis of Perfluorinated Polyimides
for Optical Applications

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Introduction

Polymers are expected to be used as media for transmitting near-infrared light in such optical communication applications as the waveguide in opto-electronic integrated circuits (OEIC) and in multichip interconnections^{1,2)}. The current manufacturing process for ICs and multichip modules includes soldering at 260 °C and short-term processes at temperature of up to 400 °C. Waveguide polymeric materials should therefore have high thermal stability - that is, a high glass transition temperature (T_g) and a high polymer decomposition temperature - as well as high transparency at the wavelengths of optical communication (WOC), 1.0-1.7 μm .

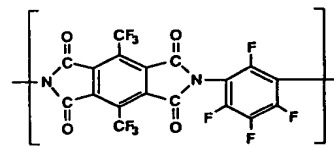
Conventional waveguide polymeric materials, such as poly(methyl methacrylate) (PMMA) or polycarbonates (PC), do not have such thermal stability. In addition, their optical losses at the WOC are much higher than in visible region (0.4-0.8 μm), because carbon-hydrogen bonds (C-H bonds) harmonically absorb infrared radiation. Two or more types of C-H bonds in PMMA and PC - those in methyl, methylene, methyne, and phenyl groups - give broad and strong absorption peaks in the infrared region. Conventional thermally stable polymers like polyimides, on the other hand, have been investigated as optical waveguide materials³⁻⁵⁾. It has been reported that optimally cured partially fluorinated polyimides can be used to decrease optical losses below 0.1 dB/cm at 0.63 μm , and that these polyimide's losses are stable at temperature of up to 200 °C⁵⁾. As described below, however, they also have some absorption peaks that originate from the C-H bonds in their phenyl groups.

The substitution of hydrogen atoms by deuterium (D) or fluorine (F) decreases optical losses in the visible region^{6,7)}. Although this effect must be greater at longer wavelengths, perdeuteration would nonetheless seem inadequate for decreasing optical losses over the entire WOC. The absorption due to the harmonics of carbon-deuterium bonds is less than that due to C-H bonds, but the third harmonics of C-D bond stretching appearing at 1.55 μm ⁸⁾ is not negligible. On the other hand, perfluorinated amorphous polymers, such as Cytop^R (Asahi Glass Co.), have been reported to have no absorption peaks between 1.0 and 2.5 μm ⁹⁾.

The combination of low optical losses in the near-infrared region and high thermal stability has therefore to be attained by the perfluorination of polyimides. This study reports the first synthesis of perfluorinated polyimides.

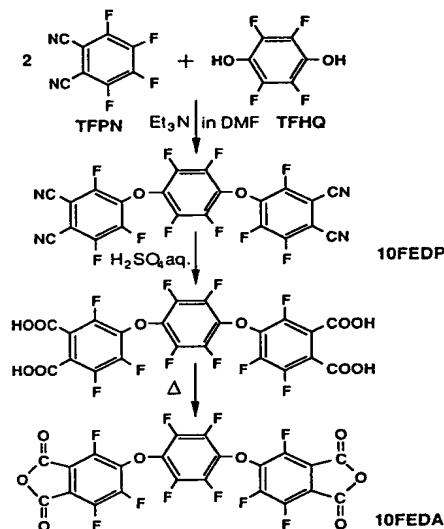
Results and Discussion

Because of the high electronegativity of fluorine, the substitution of fluorine for all the hydrogens of aromatic diamines (except for those in amino groups) considerably decreases reactivity for acylation. The electron donating properties, which reflect the reactivity for acylation^{10,11)}, of five kinds of diamines (shown in Fig.1) were estimated from ¹⁵N and ¹H NMR chemical shifts. Of these five diamines, tetrafluoro-m-phenylenediamine (4FMPD) showed the highest reactivity¹²⁾. Then the only existing perfluorinated dianhydride¹³⁾, 1,4-bis(trifluoromethyl)-pyromellitic dianhydrides (P6FDA), was used to synthesize a perfluorinated polyimide with 4FMPD by a conventional method (same as that described below). The perfluorinated polyimide (P6FDA/4FMPD, Structure 1) was, however, brittle and did not form a continuous film. This was due to the inflexibility of its molecular structure. Because the introduction of fluorine into dianhydrides, on the other hand, is expected to increase the reactivity for acylation¹²⁾, tough and flexible films of perfluorinated polyimides can be obtained by combining diamines, which have relatively high reactivities, with dianhydrides, which have flexible molecular structures.



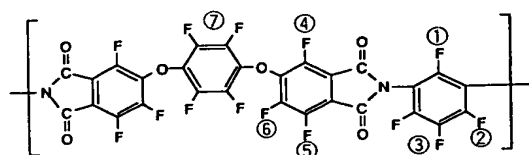
Structure 1. P6FDA/4FMPD

A novel perfluorinated dianhydride, 1,4-bis(3,4-dicarboxytrifluorophenoxy)-tetrafluorobenzene dianhydride (10FEDA), was synthesized according to the Scheme 1. This molecule has two ether-linkages which give flexibility to the molecular structure. Tetrafluorophthalonitrile (TFPN) and tetrafluorohydroquinone (TFHQ) was stirred at room temperature, in the presence of triethylamine, in dimethylformamide (DMF). This reaction mixture was then poured into water, and the oily lower layer was extracted and washed again with water. This substance was recrystallized from methanol to afford 1,4-bis(3,4-dicianotrifluorophenoxy)-tetrafluorobenzene (10FEDP). The 10FEDP was then stirred in 80% sulfuric acid at 200 °C. After cooling the acid to room temperature, the precipitated white solids were filtered and quickly washed with water, and dried. The chemical shifts and signal ratios observed using ¹⁹F NMR spectroscopy were consistent with the assigned structure. A dianhydride of 10FEDA thus obtained and a diamine of 4FMPD from Fuji Chemical Industries Ltd. were purified by sublimation under reduced pressure.



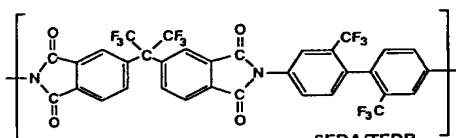
Scheme 1.

Equimolar amounts of 10FEDA and 4FMPD were added to N,N-dimethylacetamide (DMAc) (to a concentration of 15wt%) and stirred at room temperature for 7 days under nitrogen. The solution of poly(amic acid) was spin-coated onto a silicon wafer and heated first at 70 °C for 2 hours, then at 160 °C for 1 hour, at 250 °C for 30 minutes, and finally at 350 °C for 1 hour. The perfluorinated polyimide thus obtained (10FEDA/4FMPD, Structure 2) was a tough and flexible film, pale yellow like Kapton^R. This film was not soluble in polar organic solvents, such as N-methyl-2-pyrrolidinone (NMP), acetone, DMF, and DMAc. The infrared spectrum of the film (Fig. 2) had an absorption peak specific to imide groups at 1760 cm^{-1} and no peaks due to C-H bonds (around 3000 cm^{-1}). This film, with a T_g of 301 °C measured by thermal mechanical analyzer (TMA), has sufficient thermal stability above the soldering temperature. Thermal gravimetric analysis showed the initial polymer decomposition temperature was 407 °C. This measurement was conducted with a heating rate of 10 °C/min under nitrogen. At 10 kHz, the dielectric constant of the film was 2.8.



Structure 2. 10FEDA/4FMPD

Furthermore, the 10FEDA/4FMPD film cured at 200 °C (stepwise at 70 °C for 2 hours, at 160 °C for 1 hour, and at 200 °C for 2 hours) was soluble in polar organic solvents. The ^{19}F NMR spectrum of 10FEDA/4FMPD dissolved to a concentration of 5 wt% in acetone- d_6 (Fig. 3) also confirmed the completion of imidization at 200 °C. The signals appeared in the spectrum can be completely assigned. The visible-near-infrared absorption spectrum of the 10FEDA/4FMPD, cured at 200 °C and dissolved in acetone- d_6 (10 wt%), was measured with a 10-mm cell (Fig. 4). The same amount of acetone- d_6 was used as a reference. A solid line indicates the absorbance of 10FEDA/4FMPD and a dashed line indicates that of partially fluorinated polyimide (6FDA/TFDB¹⁴), Structure 3). Except for a small absorption peak due to moisture absorbed in the solvent or adsorbed on the polyimide film, the perfluorinated polyimide has no substantial absorption peak over the entire WOC. Partially fluorinated polyimide, on the other hand, has an absorption peak due to 3-fold overtone of the stretching vibration of the C-H bond (1.1 μm), a peak due to the combination of a 2-fold overtone of stretching vibration and deformation vibration of the C-H bond (1.4 μm), and a peak due to 2-fold overtone of stretching vibration of the C-H bond (1.65 μm).



Structure 3. 6FDA/TFDB

Using 10FEDA as a dianhydride, diamines of 8FODA and 8FSDA (Fig. 1) also gave continuous and flexible films. Their physical properties are similar to those of 10FEDA/4FMPD, and they will be discussed in the presentation.

Conclusion

Perfluorinated polyimides that have T_g 's over 260 °C and high optical transparency over the entire optical communication wavelengths were synthesized. Their high thermal stability and optical transparency are due to their fully aromatic molecular structure and the absence of C-H bonds. The use of diamines, which have relatively high reactivity, and the new perfluorinated dianhydride, which has flexible structure, makes it possible to obtain tough and flexible perfluorinated polyimide films. In addition, these polymers have low dielectric constants. Perfluorinated polyimides are promising for use as opto-electronic materials.

References

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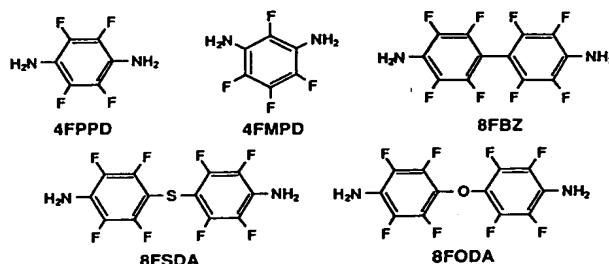


Figure 1. Structures of Diamines

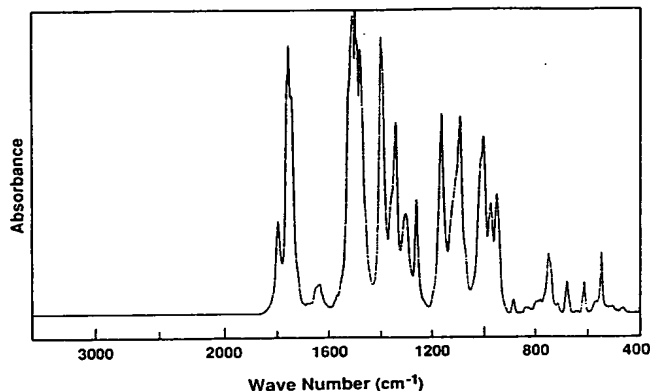


Figure 2. IR Spectrum of 10FEDA/4FMPD film

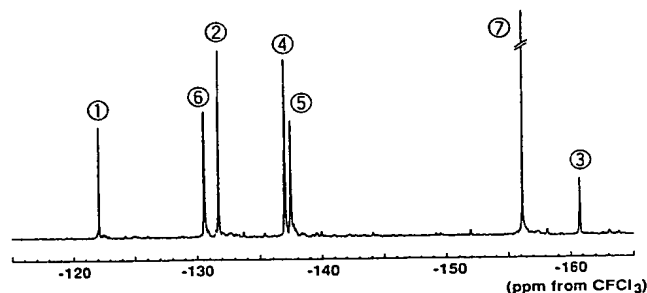


Figure 3. ^{19}F NMR Spectrum of 10FEDA/4FMPD dissolved in acetone- d_6

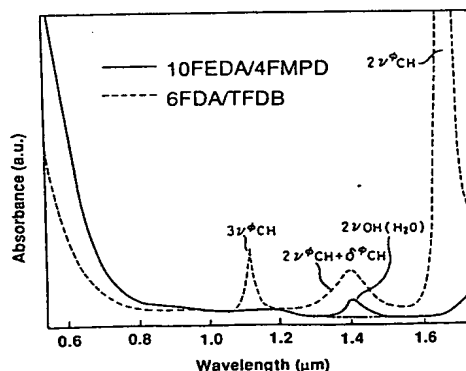


Figure 4. Visible-near-infrared Absorption Spectrum of 10FEDA/4FMPD and 6FDA/TFDB dissolved in acetone- d_6